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Comparing atmospheric $[HO_2]/[OH]$ to modeled $[HO_2]/[OH]$: Identifying discrepancies with reaction rates

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Abstract. Reactions that inter-convert OH and HO_2 are directly involved in the catalytic removal of O_3 in the lower stratosphere and in the catalytic production of O_3 in the upper troposphere. The agreement between the measured and modeled $[HO_2]/[OH]$ tests our current understanding of this important chemistry. Recent changes to the recommended rate constants for $OH+O_3$ and HO_2+O_3 call into question how accurately the chemistry of the stratosphere is understood. $[HO_2]/[OH]$ calculated with the new recommendations is 48% higher than the observations throughout the lower stratosphere, exceeding the uncertainty limits of the observations (20%). The extensive atmospheric data set allows tests of the rates of the individual processes that couple these free radicals. This work shows that the discrepancy is largest when the ratio is controlled by the reactions of OH and HO_2 with ozone.

Introduction

The partitioning of HO_x (OH and HO_2) is controlled by fast cycling reactions that inter-convert OH and HO_2 (Table 1). These reactions are significantly faster than the primary sources and sinks of HO_x so that the relative concentration of HO_2 and OH can be described accurately in terms of cycling reactions alone. In the lower stratosphere, reactions with NO and O_3 control the partitioning, while reactions with CO and NO dominate in the troposphere. The major role of these reactions in the catalytic removal of ozone in the lower stratosphere and in the production of ozone in the upper troposphere makes the quantitative understanding of these processes important [*Cohen et al.*, 1994].

An expression for the ratio of HO_2/OH is given by the ratio of rates that convert $OH \rightarrow HO_2$ to the rates that convert $HO_2 \rightarrow OH$. This description includes small contributions from the halogen oxides (ClO and BrO) and CH_4 reactions summarized in Table 1:

$$\frac{[HO_2]}{[OH]} = \frac{k_{OH+O_3}[O_3] + k_{OH+CO}[CO] + 1.7 * k_{OH+CH_4}[CH_4] + \ldots}{k_{HO_2+O_3}[O_3] + k_{HO_2+NO}[NO] + k_{HO_2+ClO}[ClO] + \ldots} \quad (1)$$

Throughout most of the lower stratosphere, the effects of halogen reactions contribute <10% of the total inter-conversion rate. The reaction of OH + CH_4 produces ~1.7 HO_2 radicals [*Hanisco et al.*, 2000], and accounts for ~8% of the $OH \rightarrow HO_2$ rate in the upper troposphere and ~3% in the lower stratosphere.

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The agreement between the measured and modeled ratios reflects our current understanding of the sum of the terms in Eq 1 and our understanding of the chemistry involved in catalytic ozone loss and production in the atmosphere [*Cohen et al.*, 1994; *Wennberg et al.*, 1998]. The variability in the atmospheric constituents that control the partitioning of OH and HO_2 (O_3, NO, CO, ...) allows errors in the individual terms of Eq 1 to be isolated. In this letter we compare the calculated to measured $[HO_2]/[OH]$ using the most recent atmospheric rate constants (*JPL*-00) [*Sander et al.*, 2000] and the earlier evaluation (*JPL*-97) [*DeMore et al.*, 1997]. Discrepancies between the two are then discussed to highlight our understanding of the chemistry in the atmosphere and to determine the areas where further detailed studies would be most beneficial.

Measurements

The *in situ* measurements presented here were obtained during the 1994-1997 NASA ER-2 field campaigns. The ASHOE/MAESA mission deployed from Christchurch, New Zealand (44°S, 172°E) in 1994. The STRAT campaign deployed from Barbers Point, HI (21°N, 155°W) and Moffett Field, CA (37°N, 122°W) in 1995-1996. The POLARIS mission deployed from Fairbanks, Alaska (65°N, 148°W) in 1997. Collectively, these observations span large variations in atmospheric conditions, having been obtained during all four seasons and over a wide range of altitude (10-21 km) and latitude (70°S to 90°N).

The instrument used for the measurement of OH and HO_2 on the ER-2 research aircraft is described in detail by *Wennberg et al.* [1994]. OH is measured by laser induced fluorescence (LIF) with an accuracy of ±25% (2σ), and an instrument precision of $\pm 1 \times 10^4$ molecules/cm^3 (typically ~1%) for a 1 min. averaging period. HO_2 is measured by chemical conversion to OH using NO, with the OH subsequently detected by LIF. The measurement accuracy of HO_2 is ±30% (2σ), with an instrument precision of $\pm 2 \times 10^4$ molecules/cm^3 (typically ~0.5%) for 1 min. averaged data. Because HO_2 is measured by chemical conversion to OH, the accuracy of the measured $[HO_2]/[OH]$ is insensitive to the calibration of the instrument to OH and depends primarily upon the uncertainty in the conversion efficiency of HO_2 to OH within the instrument (approximately ±20%) [*Cohen et al.*, 1994;

Table 1. HO_x Partitioning Reactions

Conversion of $OH \rightarrow HO_2$	Conversion of $HO_2 \rightarrow OH$
$OH + O_3 \rightarrow HO_2 + O_2$	$HO_2 + O_3 \rightarrow OH + 2O_2$
$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	$HO_2 + NO \rightarrow OH + NO_2$
$OH + ClO \rightarrow HO_2 + Cl$	$HO_2 + ClO \rightarrow HOCl + O_2$
	$HOCl + h\nu \rightarrow OH + Cl$
$OH + CH_4 \rightarrow \rightarrow CH_2O + HO_2$	$HO_2 + BrO \rightarrow HOBr + O_2$
$CH_2O + h\nu \rightarrow \rightarrow 0.7\ HO_2$	$HOBr + h\nu \rightarrow OH + Br$

Table 2. ER-2 Measurements for HO_2/OH Analysis

Species	Uncertainty	Reference
OH	±25% ±.01pptv (2σ)	*Wennberg et al.*, [1994]
HO_2	±30% ±.02pptv (2σ)	*Wennberg et al.*, [1994]
O_3	± 5%	*Proffitt et al.*, [1989]
NO	± 6%+4pptv	*Fahey et al.*, [1989]
CO	±10%	*Webster et al.*, [1994]
CH_4	± 5%	*Webster et al.*, [1994]
ClO	± 15%	*Brune et al.*, [1989b]
BrO	± 15%	*Brune et al.*, [1989a]
Pressure	± 0.25 mbar	*Chan et al.*, [1989]
Temp. (K)	± 0.3 K	*Chan et al.*, [1989]

Wennberg et al., 1994]. Nothing has changed in the instrument configuration over the three missions that would bias the conversion efficiency over time. All of the molecular species in Eq 1 that govern HO_2/OH are measured on the ER-2. These are summarized with pressure and temperature measurements in Table 2 (experimental uncertainties are included). BrO is inferred from the empirical BrO-N_2O relationship [*Wamsley et al.*, 1998] determined during the ASHOE/MAESA campaign.

Results

The comparisons between the calculated and measured [HO_2]/[OH] in the troposphere (*a*) and stratosphere (*b*) are shown in Figure 1 using both the *JPL*-97 and *JPL*-00 evaluations. In the upper troposphere, the difference between the calculations using the two recommendations is small (<3%) because the conversion of OH→HO_2 in the upper troposphere is dominated by OH+CO (R_{OH+CO}) and the conversion of HO_2→OH depends almost entirely upon HO_2+NO (R_{HO_2+NO}). The rate constants of these reactions are the same in *JPL*-97 and *JPL*-00. The mean value of the calculated ratio using either the *JPL*-97 or *JPL*-00 evaluations is ~7% greater than the measured ratio in the troposphere. The mean uncertainty of the calculated ratio is ~110%, mostly due to the large uncertainty of k_{OH+CO} (~100%). The uncertainties in the calculated ratio are determined by adjusting the reaction rate constants and *in situ* measurements for the relevant terms to their 1σ uncertainty limits and then calculating the weighted root sum of the squares of the uncertainties. Data in the troposphere show more scatter than in the stratosphere because of decreased precision resulting from lower mixing ratios of OH and HO_2 and higher background noise at lower altitude.

In the stratosphere, the ratio differs substantially between the *JPL*-97 and *JPL*-00 calculations. The mean value of the calculated ratio using *JPL*-97 is 14% higher than the measured ratio. The calculation using *JPL*-00 is 48% higher than the observations, well outside the 20% uncertainty limits of the [HO_2]/[OH] observations. However, all data are within the uncertainties of the calculated ratio, ~125% (*JPL*-97) and ~90% (*JPL*-00). The large difference between the *JPL*-97 and *JPL*-00 cases results from the importance that k_{OH+O_3} and $k_{HO_2+O_3}$ play in the stratosphere, where concentrations of O_3 are high. The OH+O_3 reaction (R_{OH+O_3}) accounts on average for ~95% of the OH→HO_2 conversion and the HO_2+O_3 reaction ($R_{HO_2+O_3}$) accounts for 36% (*JPL*-97) and 31% (*JPL*-00) of the HO_2→OH conversion rate respectively. The combined effect of an increase of ~25% in the numerator term k_{OH+O_3} and decrease of ~25% in the denominator term $k_{HO_2+O_3}$ at stratospheric temperatures is a shift of +33% in the calculated ratio of [HO_2] to [OH].

The contributions of each individual rate to the total error in the calculated [HO_2]/[OH] can be isolated by restricting data so that [HO_2]/[OH] is most sensitive to the terms in question. Figure 2 shows the fractional error of the ratio calculated from Eq 1 plotted versus the fractional contribution of the rate of OH+O_3 (r_{OH+O_3}) in (*a, b*) and the rate of HO_2+O_3 ($r_{HO_2+O_3}$) in (*c, d*) to the total inter-conversion rate of OH and HO_2 (r_{total}). The *JPL*-97 rate constants are used in all panels with the exception of *JPL*-00 k_{OH+O_3} in (*b*) and *JPL*-00 $k_{HO_2+O_3}$ in (*d*) (the upper trace in (*d*) utilizes both *JPL*-00 k_{OH+O_3} and *JPL*-00 $k_{HO_2+O_3}$). The fractional error is expressed as $E = ([HO_2]/[OH]_{calc} - [HO_2]/[OH]_{meas})/[HO_2]/[OH]_{meas}$ and the fractional contribution of each rate is expressed as $X = r_{OH+O_3}/r_{total}$ or $X = r_{HO_2+O_3}/r_{total}$. The results of each regression are used to estimate the systematic error in each ratio of rates (see *Cohen et al.*, [2000]). The measurement uncertainty is determined by adding the weighted uncertainties in quadrature, i.e. $\sigma^2 = \sigma^2_{HO_2/OH} + a_1^2\sigma^2_{NO} + a_2^2\sigma^2_{CO} + \ldots$, where a_i are the fractional weighting terms.

In panels (*a, b*) the data are restricted so that HO_2+O_3 is <10% and HO_2+ClO and HO_2+BrO combined are <5% of the total conversion rate of HO_2→OH. The total uncertainties (weighted error from the measurement uncertainties and rate constants) from these terms are included with the measurement uncertainty. With this restriction, the ratio is dominated by the flux in three reactions:

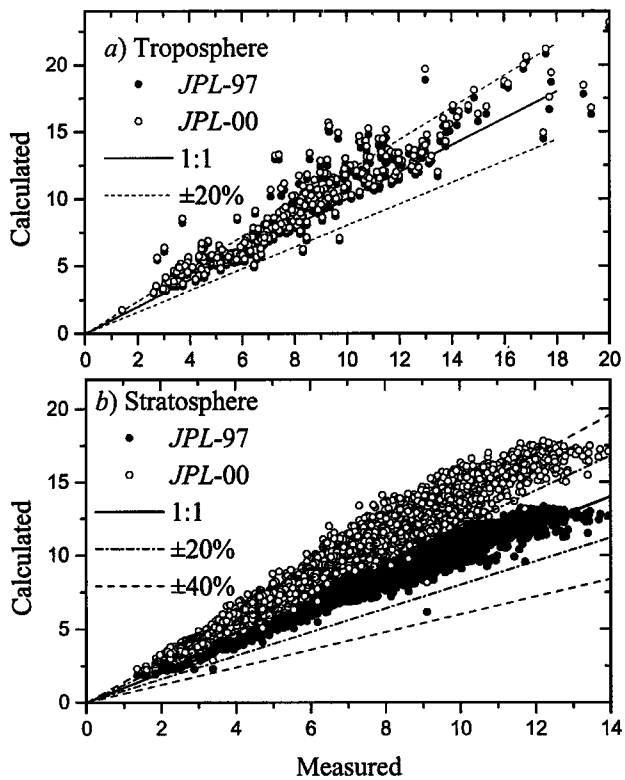

Figure 1. Measured [HO_2]/[OH] versus the calculated ratio using *JPL*-97 and *JPL*-00 for (*a*) tropospheric (STRAT) and (*b*) stratospheric (ASHOE/MAESA and POLARIS) data averaged at 1 min. intervals. Tropospheric data were restricted with the criteria $r_{OH+CO} > 5\times r_{OH+O_3}$ and NO > 50 pptv. Stratospheric data are restricted with the criteria SZA < 80° and air number density < 2.5×10^{18} molecules cm^{-3}. The dashed lines show the 20% uncertainty of the [HO_2]/[OH] measurement. The 40% error bars are shown for reference in (*b*).

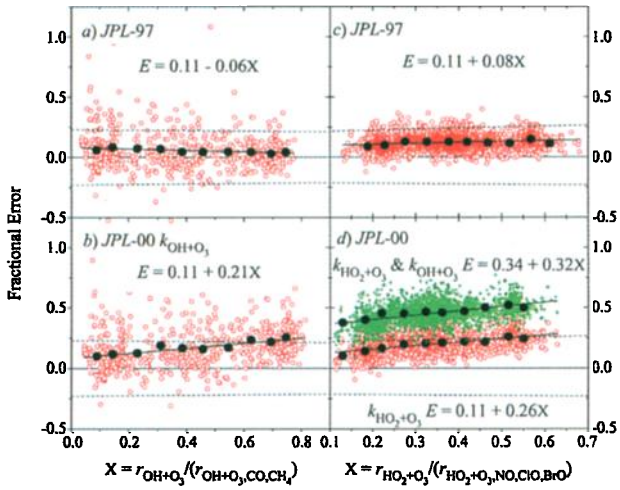

Figure 2. The fractional error in the calculated $[HO_2]/[OH]$ is plotted versus the fractional contribution of $OH+O_3$ (*a, b*) and HO_2+O_3 (*c, d*) to the total inter-conversion rate between OH and HO_2. *JPL*-97 rates are used throughout, except in (*b*) *JPL*-00 k_{OH+O_3} is used and in (*d*) *JPL*-00 $k_{HO_2+O_3}$ is used. The data in (*a, b*) are restricted by NO > 50 pptv. Additional constraints are that $r_{HO_2+O_3}$ is less than 10% of the total inter-conversion rate of $HO_2 \rightarrow OH$ and $T = 205 \pm 10K$. The data in (*c, d*) are restricted as in Figure 1*b*. Additional constraints are that r_{HO_2+ClO} and r_{HO_2+BrO} each contribute less than 10% to the total inter-conversion rate of $HO_2 \rightarrow OH$ and that $T = 225 \pm 10K$. The temperature in each panel was chosen to span the widest range of the rate being tested. Data are averaged at 1 min. intervals (small dots) and into 10 bins of the *x*-coordinate (large dots). The lines are linear fits to the 1 min. data. The dashed lines represent the uncertainties determined from all of the measurement uncertainties as well as the weighted uncertainties of k_{HO_2+ClO} and k_{HO_2+BrO}. The upper trace in Figure 2 (*d*) shows the fractional error when both *JPL*-00 k_{OH+O_3} and *JPL*-00 $k_{HO_2+O_3}$ are used.

$$\frac{[HO_2]}{[OH]} \approx \frac{k_{OH+O_3}[O_3] + k_{OH+CO}[CO]}{k_{HO_2+NO}[NO]} \qquad (2)$$

When $X_{OH+O3} = 0$, the ratio is essentially determined by R_{OH+CO} and R_{HO_2+NO} so that the error ($E_{X=0}$) can be ascribed to $k_{OH+CO}[CO]/k_{HO_2+NO}[NO]$. Note that the uncertainties in the measurements (CO, NO, and O_3) are included in the total measurement uncertainty, which is dominated by the uncertainty in HO_2/OH. When $X_{OH+O_3} = 1$, the ratio is described by R_{OH+O_3} and R_{HO_2+NO} and the error ($E_{X=1}$) is from $k_{OH+O_3}[O_3]/k_{HO_2+NO}[NO]$. The slope is equal to the difference in the errors of $k_{OH+CO}[CO]$ and $k_{OH+O_3}[O_3]$. In panel (*a*) $E = 0.11(1) - 0.06(3)X_{OH+O_3}$, where the values in parenthesis are the statistical uncertainties of the least significant figures determined from the regression. With the uncertainty from the *in situ* measurements included, the errors determined using the *JPL*-97 evaluation are: $E_{X=0} = 0.11 \pm 0.24$, and $E_{X=1} = 0.05 \pm 0.24$. In panel (*b*) $E = 0.11(1) + 0.21(3)X_{OH+O_3}$. The errors using the *JPL*-00 evaluation for k_{OH+O_3} are: $E_{X=0} = 0.11 \pm 0.24$, and $E_{X=1} = 0.32 \pm 0.24$. The absolute difference between the slopes in each panel (0.27 ± 0.03) is equal to the difference in the rate constants of k_{OH+O_3} at 205 K (*JPL*-00 is 26% higher than *JPL*-97).

In panels (*c, d*) the data are restricted so that OH+CO contributes less than 5% of the total $OH \rightarrow HO_2$ rate and HO_2+ClO and HO_2+BrO contribute less than 10% of the total $HO_2 \rightarrow OH$ rate. The weighted uncertainties from these terms are included with the measurement uncertainty. With these restrictions the ratio is determined primarily by:

$$\frac{[HO_2]}{[OH]} \approx \frac{k_{OH+O_3}[O_3]}{k_{HO_2+O_3}[O_3] + k_{HO_2+NO}[NO]} \qquad (3)$$

When $X_{HO_2+O_3} = 0$, the ratio is controlled by R_{OH+O_3} and R_{HO_2+NO} and the error ($E_{X=0}$) is from $k_{OH+O_3}[O_3]/k_{HO_2+NO}[NO]$. When $X_{HO_2+O_3} = 1$, the ratio is described by R_{OH+O_3} and $R_{HO_2+O_3}$ and the error ($E_{X=1}$) is from $k_{OH+O_3}[O_3]/k_{HO_2+O_3}[O_3]$. The inverse slope is equal to the difference in the error in both $k_{HO_2+O_3}[O_3]$ and $k_{HO_2+NO}[NO]$ (inverse because these are denominator terms). In panel (*c*) $E = 0.11(0) + 0.06(1)X_{HO_2+O_3}$. The errors using the *JPL*-97 rate constants are: $E_{X=0} = 0.11 \pm 0.21$, and $E_{X=1} = 0.17^{+0.29}_{-0.24}$. In panel (*d*) $E = 0.11(0) + 0.26(1)X_{HO_2+O_3}$. The errors using the *JPL*-00 rate constant for $k_{HO_2+O_3}$ are: $E_{X=0} = 0.11 \pm 0.21$, and $E_{X=1} = 0.37^{+0.29}_{-0.24}$. The absolute difference between the slopes in panel (*c*) and panel (*d*) (0.20 ± 0.01) is equal to the difference in the rates of $k_{HO_2+O_3}$ at 225 K (*JPL*-97 is 22% higher than *JPL*-00). When *JPL*-00 k_{OH+O_3} is included in panel *d* (upper trace), *E* is higher by 0.23, and the corresponding errors increase to: $E_{X=0} = 0.34 \pm 0.21$, and $E_{X=1} = 0.66^{+0.29}_{-0.24}$. For this case, when $X_{HO_2+O_3} = 1$ and the ratio is controlled solely by $R_{OH+O_3}/R_{HO_2+O_3}$, the error is 66%, 42% beyond the combined uncertainties of the measurements and remaining rate constants (±24%: dashed line in all panels of Figure 2). The results of Figure 2 are summarized in Table 3.

Discussion and conclusions

The good agreement observed in Figure 2(*a*) and 2(*c*) could be fortuitous. The NO, CO, and O_3 measurements could have offsetting errors; k_{OH+CO}, k_{OH+O_3}, and k_{HO_2+NO} could all be high by the same amount; or some combination of offsetting errors in both the *in situ* measurements and rate constants could be present. However, the ratio of rate constants in Figure 2(*a*) and (*c*) suggest that if any single rate constant in the *JPL*-97 recommendation is accurate then the other rate constants are accurate to within the uncertainties of the *in situ* measurements.

When the *JPL*-00 recommendation for both k_{OH+O_3} and $k_{HO_2+O_3}$ are used (upper trace in Figure 2(*d*)), and when $X_{HO_2+O_3} = 1$, the calculated $[HO_2]/[OH]$ disagrees with *in situ* observations by 66%, well beyond the uncertainties in the observations. The 66%

Table 3. Errors in the rate constants determined from regressions of the fractional error of calculated $[HO_2]/[OH]$ versus X_{OH+O_3} and $X_{HO_2+O_3}$ in Figure 2. The uncertainties include the measurement uncertainty of $[OH]/[HO_2]$ and the weighted uncertainties from the unregressed rates ie. $k_{HO_2+ClO}[ClO]$, $k_{HO_2+BrO}[BrO]$, and $k_{OH+CH_4}[CH_4]$. Uncertainties of the slope errors, (dE/dX), eg., the difference in the errors of $k_{OH+O_3}[O_3]$ and $k_{OH+CO}[CO]$, do not include the uncertainty of the measured $[HO_2]/[OH]$.

	$X = r_{OH+O_3}/r_{total}$		$X = r_{HO_2+O_3}/r_{total}$	
	JPL-97	JPL-00	JPL-97	JPL-00
dE/dX	-0.06±0.12	0.21±0.12	0.06±0.12	0.26±0.12
$E_{X=0}$	0.11±0.24	0.11±0.24	0.11±0.21	0.34±0.21
$E_{X=1}$	0.05±0.24	0.32±0.24	$0.17^{+0.29}_{-0.24}$	$0.66^{+0.29}_{-0.24}$

discrepancy at $X_{HO_2+O_3} = 1$ in Figure 2*(d)* suggests one or more of the following: our understanding of HO_x partitioning is incomplete; the measured $[HO_2]/[OH]$ is in error (too low); $k_{OH+O_3}/k_{HO_2+O_3}$ using *JPL*-00 is in error (too high); or some combination. Eq 1 does not include every reaction that cycles HO_x. However, a comparison of the ratio determined from a numerical integration of a model that contains a more complete representation of the photochemistry (e.g. *Salawitch et al.*, [1994]) and the ratio determined from Eq 1 using the inputs from the complete model shows that Eq 1 underpredicts HO_2/OH by 3±1% compared to the full model. Thus, our use of a simplified model approach cannot be responsible for the discrepancy between measured and modeled HO_2/OH. While missing chemistry cannot be excluded as a possible explanation, this is unlikely because it would have to compete on the same time scale as the reactions in Table 1. Missing chemistry that would decrease calculations of $[HO_2]/[OH]$ by 66% requires one or more chemical species that converts $HO_2 \rightarrow OH$. For a second order rate constant of $\sim 1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, an unidentified molecule(s) would have to be present at 350 pptv. Because no direct *in situ* intercomparisons with other HO_x measurements are available, we can offer no independent verification for the measured $[HO_2]/[OH]$. However, other $[HO_2]/[OH]$ studies show similar agreement to the results presented here using the *JPL*-97 recommendation [*Brune et al.*, 1999]. Errors in the other *in situ* measurements cannot be ruled out, either. However, separate analyses of $[NO]/[NO_2]$ have shown the NO and O_3 measurements used in these calculations to be consistent with two independent measurements of NO_2 and the appropriate rate constants [*Cohen et al.*, 2000; *Del Negro et al.*, 1999].

As noted in the *JPL* recommendations, laboratory measurements of the rate constants for $OH+O_3$ and HO_2+O_3 at temperatures similar to the upper troposphere and lower stratosphere are virtually nonexistent. No measurements of HO_2+O_3 had been obtained below 240K at the time of the *JPL*-00 evaluation. This is reflected in the uncertainty assigned to these rate constants in the *JPL* recommendation ($k_{OH+O_3} \sim \pm 0.34$ at 225 K and $k_{HO_2+O_3} \sim {}^{+0.50}_{-0.34}$ at 225 K). Recent measurements (completed after the *JPL*-00 evaluation) by *Herndon et al.*, [2000] of $k_{HO_2+O_3}$ at low temperatures (200-298 K) and a range of pressures (50-200 torr) agree well with the *JPL*-97 recommendation at 225 K. Additionally, recent work by *Nizkorodov et al.*, [2000] measures the sum of k_{OH+O_3} and $k_{HO_2+O_3}$ over the temperature range 190-315 K. The k_{OH+O_3} derived by subtracting $k_{HO_2+O_3}$ from the sum of the rate constants determined in this study lies between the *JPL*-97 and *JPL*-00 recommendation.

The extensive data set of atmospheric observations allows a comprehensive quantitative analysis of HO_2/OH throughout the lower stratosphere. The analysis in this letter shows a large discrepancy between the measured to modeled HO_2/OH when *JPL*-00 rate constants are used in the calculations. This discrepancy correlates with the fractional contribution of O_3 in the inter-conversion of OH and HO_2. If the measurements and model are accurate, then the rate constants could be the source of the discrepancy. These facts, coupled with the importance of the HO_2+O_3 reaction as the rate limiting step in the direct catalytic loss of ozone by HO_x, points to the need for continued effort to improve the chemical kinetic database at temperatures and pressures relevant to the upper troposphere and lower stratosphere.

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